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Palladium-Catalyzed Annulation of 2,2′-Dibromobiphenyls with Alkynes: Synthesis of Functionalized Phenanthrenes and Dibenzochrysenes

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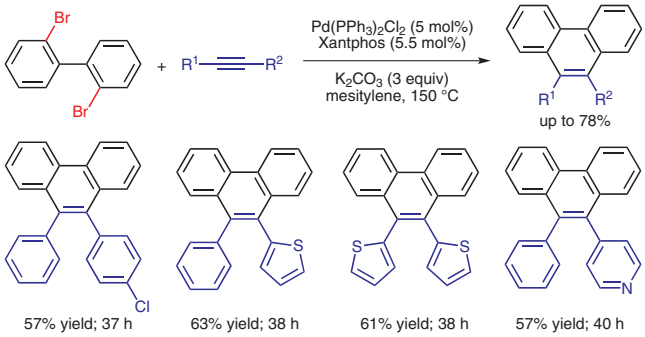

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Abstract A palladium-catalyzed annulation process of 2,2′-dibromobiphenyls with alkynes for the synthesis of functionalized phenanthrenes has been realized. The methodology provides an efficient approach to dibenzochrysene derivatives starting from simple reactants in two steps.

Key words alkynes, annulations, domino reaction, fused-ring systems, palladium

Because of the advances in organic electronics such as light emitters, semiconductors, liquid crystals, and solar cells, the chemistry of polycyclic aromatic hydrocarbons (PAHs) has attracted a great deal of attention and they have become increasingly important for the development of superior organic materials.[1] Phenanthrene is one of the most stable fused aromatics.[2] Its high resonance energy and high energy gap qualify it as a highly attractive building block for conjugated systems. Many π-conjugated functional materials such as picene[3] and carbon nanotubes[4] contain a core of phenanthrene motif. Some phenanthrene derivatives have exhibited excellent photoconductivity,[5] superconductivity[3] and electroluminescent[6] properties as well as interesting biological activities such as antitumor, anti-immune and anti-inflammatory properties.[7] Phenanthrene oligomers are useful stable p-type semiconductors for organic field-effect transistors (OFETs)[8] and 9,10-diarylphenanthrenes can be converted into photoluminescent blue-emitting polyphenanthrenes.[9] Based on these promising features, development of efficient synthetic routes to the phenanthrenes bearing appropriate functional group, especially incorporating heteroatom is highly valuable for the control of the optical and electronic properties of materials.

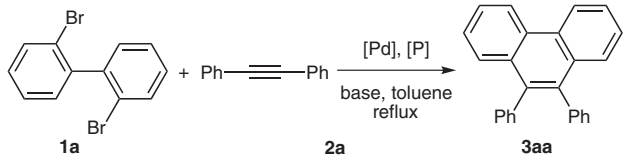
Although a number of efficient synthetic methodologies have been developed for the preparation of π-conjugated phenanthrenes,[10–15] the recently reported transition-metal-catalyzed annulations of biphenyl derivatives,[14,15] especially using 2,2′-diiodobiphenyls[15] with alkynes are the most economic and synthetically most attractive for the easily prepared or commercially available substances, low reaction cost, high efficiency and widespread functional group tolerance. However, only iodobiphenyls showed unique reactivity towards alkynes and successfully afforded the phenanthrenes; attempts of using their analogues such as 2-bromobiphenyl and 2,2′-dibromobiphenyl failed to promote the annualtion.[15b] To realize the annulation of bromobiphenyls and alkynes is still a great challenge and has become an urgent issue for the generality of this kind of methodology.

We previously reported that 1,8-dibromonaphthalene effectively underwent the annulation reaction with alkynes in the presence of a palladium catalyst to afford the corresponding annulated acenaphthylenes.[16] It may be conceived that the phenanthrene ring would be generated when 2,2′-dibromobiphenyl was used instead of 1,8-dibromonaphthalene under the similar reaction conditions. Indeed, it worked well under the optimized reaction conditions. We report herein a palladium-catalyzed annulation reaction of 2,2′-dibromobiphenyl and alkynes to synthesize functionalized phenanthrenes.

Initially, we chose 2,2′-dibromobiphenyl (**1a**) and diphenylacetylene (**2a**) as model substrates to screen the reaction (Table 1). We found that a combination of tetrakis(triphenylphosphine)palladium (5 mol%), triphenylphosphine (5.5 mol%), and potassium carbonate (3.0 equiv) in toluene at reflux successfully gave the desired annulation product 9,10-diphenylphenanthrene (**3aa**) in 20% isolated yield (Table 1, entry 1).

The screening of palladium source revealed that bis(triphenylphosphine)palladium(II) dichloride showed the best catalytic ability and enhanced the yield to 37% (Table 1, entry 4). On further examination of various bases and phosphine ligands i.e., tricyclohexylphosphine (PCy_3; Table 1, entry 8), dicyclohexyl(2′,6′-dimethoxybiphenyl-2-yl)phosphine (S-Phos; Table 1, entry 9), dicyclohexyl(2′,4′,6′-triisopropylbiphenyl-2-yl)phosphine (X-Phos; Table 1, entry 10) and (9,9-dimethyl-9*H*-xanthene-4,5-diyl)bis(diphenylphosphine) (Xantphos; Table 1, entry 11), the combination of potassium carbonate and Xantphos exhibited the highest performance and improved the yield to 59% (Table 1, entry 11). The strong base, potassium *tert*-butoxide was ineffective in this transformation and only trace product was formed (monitored by TLC plate; Table 1, entry 6). A higher reaction temperature is generally beneficial to the annulation process, especially for the synthesis of PAHs. Therefore, we used mesitylene as a solvent instead of toluene and increased the reaction temperature to 150 °C.

Table 1 Screen of Reaction Conditions[a]



Entry	[Pd]	[P]	Base	T (h)	Yield (%)[b]
1	$Pd(PPh_3)_4$	Ph_3P	K_2CO_3	48	20
2	$Pd(OAc)_2$	Ph_3P	K_2CO_3	48	30
3	$Pd_2(dba)_3$	Ph_3P	K_2CO_3	48	10
4	$Pd(PPh_3)Cl_2$	Ph_3P	K_2CO_3	48	37
5	$Pd(PPh_3)Cl_2$	Ph_3P	Cs_2CO_3	48	32
6	$Pd(PPh_3)Cl_2$	Ph_3P	*t*-BuOK	48	trace
7	$Pd(PPh_3)Cl_2$	Ph_3P	Et_3N	48	8
8	$Pd(PPh_3)Cl_2$	Cy_3P	K_2CO_3	48	12
9	$Pd(PPh_3)Cl_2$	S-Phos	K_2CO_3	48	15
10	$Pd(PPh_3)Cl_2$	X-Phos	K_2CO_3	48	19
11	$Pd(PPh_3)Cl_2$	Xantphos	K_2CO_3	48	59
12[c]	$Pd(PPh_3)Cl_2$	Xantphos	K_2CO_3	36	78

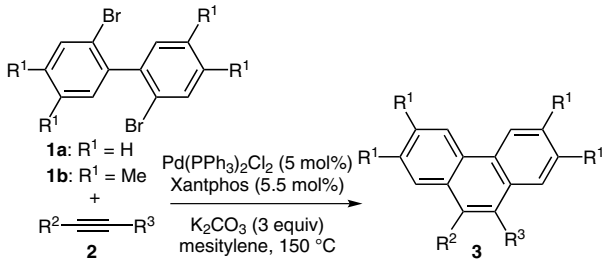
[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.33 mmol), [Pd] (5.0 mol%), ligand (5.5 mol%), base (3.0 equiv), toluene (5 mL), reflux.
[b] Isolated yield.
[c] Mesitylene was used as a solvent and the reaction temperature was increased to 150 °C (bath temp.).

As we expected, the corresponding 9,10-diphenylphenanthrene was finally obtained in 78% yield (Table 1, entry 12).

With the optimal reaction conditions in hand, we next investigated the substrate scope of the annulation reaction (Table 2). Diarylalkynes with substituent such as methyl (**2b**), ethyl (**2f**), sterically bulky *tert*-butyl (**2j**), electron-withdrawing acetyl group (**2k**) and nitro group (**2l**) and electron-donating methoxy group (**2c** and **2g**) all smoothly underwent the annualtions with 2,2′-dibromobiphenyls to produce the functionalized phenanthrenes in good yields. Electron-deficient alkynes were less reactive and gave a slightly lower yield even with a longer reaction time. Note that diarylalkynes with halo substituents such as fluoro (**2e**) and chloro (**2p**) on the benzene ring were well tolerated. The functionalized phenanthrenes containing halo atoms are very useful for they can be easily further derivatized by means of simple coupling strategies and the likes. Diarylalkyne with sterically demanding *ortho* substituent still successfully afforded the corresponding phenanthrenes (**3ad** and **3bd**) even though with sharply decreased yields. 2,2′-Dibromo-4,4′,5,5′-tetramethylbiphenyl (**1b**) furnished the annulations process in a shorter reaction time but with slightly lower yields than 2,2′-dibromobiphenyl (**1a**). Additionally, 1-aryl-2-alkyl substituted acetylenes also successfully reacted with 2,2′-dibromobiphenyl to give the corresponding phenanthrenes in high yield (**3h** and **3i**). More importantly, electron-deficient acetylenes with heteroaromatic substituents such as 1-phenyl-2-(2-thienyl)acetylene (**2m**), di(2-thienyl)-substituted acetylenes (**2n**) and 1-phenyl-2-(4-pyridyl)acetylene (**2o**) were still capable of the annulations with 2,2′-dibromobiphenyl and generated the functionalized phenanthrenes with heteroaromatics in fair yields. The synthesis of 9,10-disubstituted phenanthrene derivatives containing heteroaromatics has seldom been reported before using electron-deficient heteroaromatic-substituted acetylenes, especially when the heteroatom exists *ortho* to the substituted position of heteroaromatic ring. The successful incorporation of heteroaromatic rings in PAHs is highly valuable to the electronic and optical properties of organic materials. In fact, the incorporation of heteroaromatic rings and the fusion of bridging heteroatoms may tune the molecular and electronic structures of PAHs, which are closely related to the electronic properties of materials.

The dibenzochrysene (DBC) is a twisted polycyclic aromatic hydrocarbon. Its derivatives can be applied to the preparation of sensors, nonlinear optical and liquid-crystalline materials, etc. The preparation of parent dibenzochrysene and its derivatives generally requires multistep syntheses.[17] The Scholl reaction[18] is one of the most famous C–C bond-forming reactions and has been extensively utilized for intramolecular oxidative cyclodehydrogenation of various polybenzenoid hydrocarbons to prepare the corresponding planar polyaromatic hydrocarbons.[1a,b] To illustrate the potential application of 9,10-diarylphenanthrenes, we investigated the synthesis of dibenzochrylsenes by the Scholl reaction using **3aa** and **3ab** (Scheme 1). The dibenzochrylsenes **4aa** and **4ab** were readily synthesized with yields of 70% and 82%, respectively, using $CuCl_2$ and $AlCl_3$ as an oxidant.

Table 2 Palladium-Catalyzed Annulations of 2,2′-Dibromobiphenyls with Alkynes



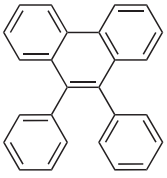
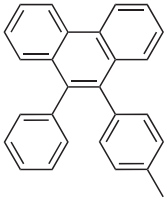
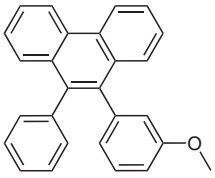
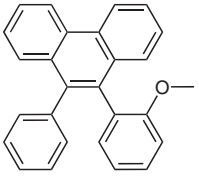
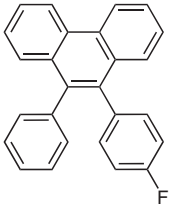
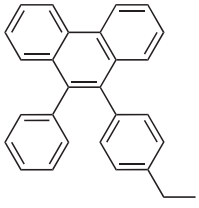
Entry	Product	Time (h)	Yield (%)
1	**3aa** 	36	78
2	**3ab** 	30	69
3	**3ac** 	30	58
4	**3ad** 	48	21
5	**3ae** 	38	53
6	**3af** 	30	72

Table 2 (continued)

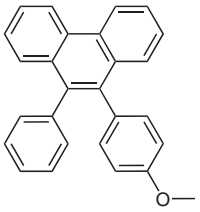
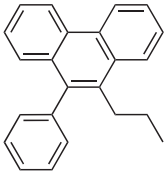
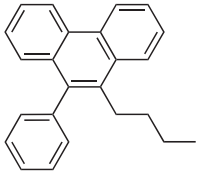
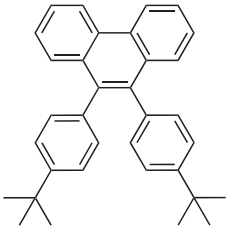
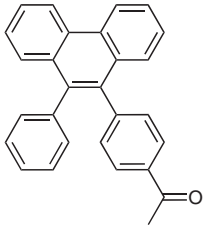
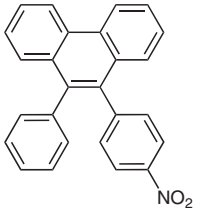
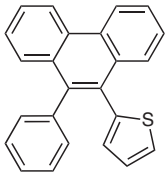
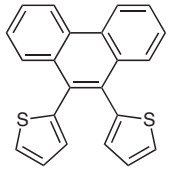
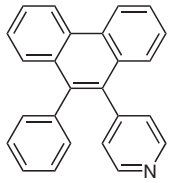
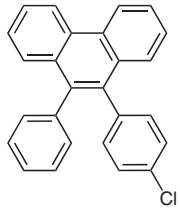
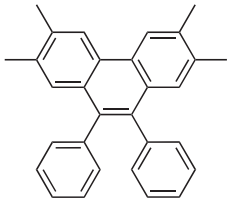
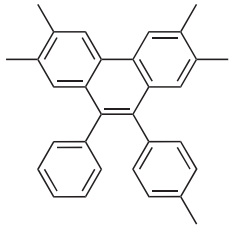
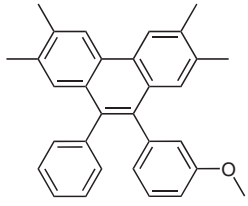
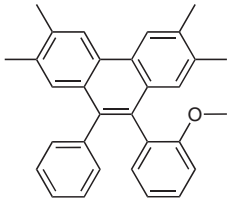
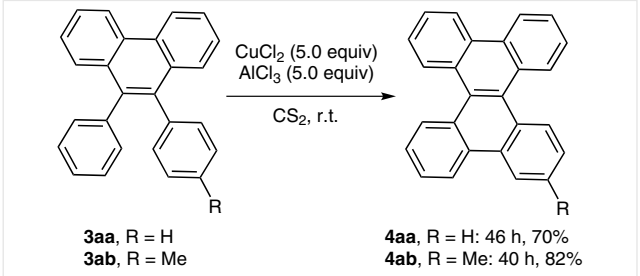
Entry	Product	Time (h)	Yield (%)
7	**3ag** 	28	61
8	**3ah** 	33	69
9	**3ai** 	33	66
10	**3aj** 	35	60
11	**3ak** 	40	59
12	**3al** 	40	43
13	**3am** 	38	63

Table 2 (continued)

Entry	Product	Time (h)	Yield (%)
14	**3an** 	38	61
15	**3ao** 	40	57
16	**3ap** 	37	57
17	**3ba** 	18	60
18	**3bb** 	14	50
19	**3bc** 	24	34
20	**3bd** 	36	10



Scheme 1 Synthesis of dibenzochrysene derivatives

In conclusion, we have developed a palladium-catalyzed annulation process of 2,2′-dibromobiphenyls with alkynes for the synthesis of functionalized phenanthrenes.[19,20] The electron-deficient heteroaromatic-substituted acetylenes are capable of the annulation process. Thiophene-fused and pyridine-fused PAHs can also be synthesized easily. This methodology also provides a highly efficient and low-cost approach to dibenzochrysene derivatives starting from simple, commercially available reactants in two steps.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1378726.

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(19) **9,10-Disubstituted Phenanthrenes 3aa–3bd; General Procedure**: A Schlenk flask was charged with 2,2′-dibromobiphenyls (0.3 mmol), alkyne (0.33 mmol), $Pd(PPh_3)_2Cl_2$ (11 mg, 5 mol%), Xantphos (10 mg, 5.5 mol%) and K_2CO_3 (124 mg, 0.9 mmol) under N_2. Mesitylene (5 mL) was added from a syringe, and the mixture was stirred at 150 °C until the reaction was complete (TLC). The mixture was cooled to r.t., and H_2O (10 mL) was added. The resulting mixture was extracted with EtOAc (3 × 15 mL). The organic layers were combined, dried over anhyd Na_2SO_4, and concentrated to give a residue that was purified by column chromatography (silica gel, PE–EtOAc).

9-(3-Methoxyphenyl)-10-phenylphenanthrene (3ac): white solid; yield: 63 mg (58%); mp189.8–191.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 8.3 Hz, 2 H), 7.60–7.68 (m, 3 H), 7.54–7.57 (m, 1 H), 7.46–7.51 (m, 2 H), 7.26–7.29 (m, 1 H), 7.18–7.25 (m, 3 H), 7.13–7.16 (m, 2 H), 6.70–6.79 (m, 3 H), 3.68 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.9, 140.9, 139.5, 137.0, 137.0, 131.9, 131.7, 131.0, 131.0, 130.0, 130.0, 128.5, 127.9, 127.7, 127.6, 126.6, 126.6, 126.5, 126.4, 123.8, 122.5, 122.5, 116.6, 112.4, 55.2. HRMS (ESI): *m*/*z* calcd for $[C_{27}H_{20}ONa]^+$: 383.1412; found: 383.1418.

9-(2-Methoxyphenyl)-10-phenylphenanthrene (3ad): faint yellow solid; yield: 23 mg (21%); mp 198.9–191.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (dd, *J* = 8.3, 4.0 Hz, 2 H), 7.53–7.58 (m, 2 H), 7.47–7.50 (m, 1 H), 7.36–7.41 (m, 3 H), 7.07–7.16 (m, 6 H), 6.93 (dd, *J* = 7.4, 1.7 Hz, 1 H), 6.68–6.77 (m, 2 H), 3.49 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.2, 138.8, 136.5, 133.0, 131.3, 131.0, 130.7, 129.7, 129.1, 128.9, 127.5, 127.5, 126.7, 126.4, 126.2, 125.6, 125.5, 125.4, 125.2, 125.2, 121.5, 121.5, 119.0, 109.3, 54.1. HRMS (ESI): *m*/*z* calcd for $[C_{27}H_{20}ONa]^+$: 383.1412; found: 383.1407.

9-(4-Fluorophenyl)-10-phenylphenanthrene (3ae): white solid; yield: 55 mg (53%); mp 256.8–257.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 8.4 Hz, 2 H), 7.64–7.68 (m, 2 H), 7.47–7.56 (m, 4 H), 7.20–7.26 (m, 3 H), 7.08–7.14 (m, 4 H), 6.90–6.95 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.8, 160.3, 139.5, 137.7, 136.1, 135.5, 132.6, 132.5, 131.8, 131.0, 130.1, 127.9, 127.7, 127.6, 126.7, 126.6, 126.6, 126.5, 122.6, 122.5, 114.7, 114.5. HRMS (ESI): *m*/*z* calcd for $[C_{26}H_{17}FNa]^+$: 371.1212; found: 371.1225.

9-(4-Ethylphenyl)-10-phenylphenanthrene (3af): white solid; yield: 77 mg (72%); mp 163.3–164.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 8.3 Hz, 2 H), 7.54–7.67 (m, 4 H), 7.45–7.50 (m, 2 H), 7.18–7.26 (m, 3 H), 7.14–7.16 (m, 2 H), 7.05 (s, 4 H), 2.61 (q, *J* = 7.6 Hz, 2 H), 1.21 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.2, 141.6, 139.7, 137.3, 137.2, 136.7, 132.1, 132.0, 131.1, 130.9, 130.0, 129.0, 128.0, 127.8, 127.6, 127.2, 127.0, 126.6, 126.3, 126.3, 122.5, 122.4, 28.5, 15.4. HRMS (ESI): *m*/*z* calcd for $[C_{28}H_{22}Na]^+$: 381.1620; found: 381.1629.

9,10-Bis(4-*tert*-butylphenyl)phenanthrene (3aj): white solid; yield: 80 mg (60%); mp 279.9–281.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 8.2 Hz, 2 H), 7.71 (dd, *J* = 8.2, 0.9 Hz, 2 H), 7.63–7.67 (m, 2 H), 7.48–7.51 (m, 2 H), 7.17–7.20 (m, 4 H), 7.01–7.03 (m, 4 H), 1.27 (s, 18 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.0, 137.6, 136.6, 132.0, 130.7, 129.9, 128.0, 126.5, 126.2, 124.1, 122.5, 34.4, 31.3. HRMS (ESI): *m*/*z* calcd for $[C_{34}H_{34}Na]^+$: 465.2559; found: 465.2572.

9-Phenyl-10-(2-thienyl)phenanthrene (3am): yellow solid; yield: 64 mg (63%); mp 214.5–215.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 8.3 Hz, 2 H), 7.78–7.80 (m, 1 H), 7.65–7.70 (m, 2 H), 7.52–7.56 (m, 2 H), 7.46–7.50 (m, 1 H), 7.22–7.33 (m, 6 H), 6.92–6.95 (m, 1 H), 6.84–6.86 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.1, 139.9, 139.5, 132.5, 131.7, 130.7, 130.4,

129.9, 129.6, 129.2, 128.2, 127.6, 127.6, 126.9, 126.9, 126.8, 126.7, 126.6, 126.3, 126.0, 122.5, 122.4. HRMS (ESI): *m*/*z* calcd for $[C_{24}H_{16}SNa]^+$: 359.0871; found: 359.0872.

4-(10-Phenylphenanthren-9-yl)pyridine (3ao): faint yellow solid; yield: 57 mg (57%); mp 235.8–236.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (dd, *J* = 8.3, 4.9 Hz, 2 H), 8.42 (dd, *J* = 4.5, 1.4 Hz, 2 H), 7.60–7.65 (m, 2 H), 7.37–7.50 (m, 4 H), 7.16–7.22 (m, 3 H), 7.01–7.08 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.2, 148.2, 138.6, 137.3, 134.4, 131.5, 130.8, 130.5, 130.2, 128.1, 128.0, 127.9, 127.1, 127.1, 127.0, 127.0, 126.9, 126.8, 126.3, 122.8, 122.6. HRMS (ESI): *m*/*z* calcd for $[C_{25}H_{17}NNa]^+$: 354.1259; found: 354.1265.

9-(*p*-Tolyl)-2,3,6,7-tetramethyl-10-phenylphenanthrene (3bb): faint yellow solid; yield: 60 mg (50%); mp 249.9–251.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 2 H), 7.11–7.24 (m, 7 H), 7.00 (s, 4 H), 2.52 (s, 6 H), 2.31 (s, 3 H), 2.30 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.3, 136.9, 135.9, 135.9, 135.5, 135.3, 135.3, 135.2, 131.2, 131.0, 130.3, 130.2, 128.2, 128.1, 128.1, 127.8, 127.7, 127.4, 126.1, 122.7, 29.7, 21.3, 20.4, 20.2, 20.2. HRMS (ESI): *m*/*z* calcd for $[C_{31}H_{28}Na]^+$: 423.2089; found: 423.2089.

9-(3-Methoxyphenyl)-2,3,6,7-tetramethyl-10-phenylphenanthrene (3bc): faint yellow solid; yield: 42 mg (34%); mp 149.1–150.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 2 H), 7.37 (s, 1 H), 7.23–7.31 (m, 7 H), 6.72–6.82 (m, 3 H), 3.72 (s, 3 H), 2.58 (s, 6 H), 2.36 (d, *J* = 6.0 Hz, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.8, 141.4, 140.1, 135.7, 135.7, 135.4, 135.4, 135.3, 131.1, 131.1, 130.1, 129.9, 128.4, 128.1, 128.1, 127.8, 127.8, 127.6, 127.4, 126.3, 123.9, 122.7, 116.6, 112.2, 55.2, 21.6, 20.5, 20.2, 15.4. HRMS (ESI): *m*/*z* calcd for $[C_{31}H_{28}ONa]^+$: 439.2038; found: 439.2035.

9-(2-Methoxyphenyl)-2,3,6,7-tetramethyl-10-phenylphenanthrene (3bd): faint yellow solid; yield: 12 mg (10%); mp 203.5–204.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 5.4 Hz, 2 H), 7.12–7.21 (m, 8 H), 7.01 (dd, *J* = 7.4, 1.7 Hz, 1 H), 6.82–6.84 (m, 1 H), 6.75 (d, *J* = 8.2 Hz, 1 H), 3.56 (s, 3 H), 2.53 (s, 3 H), 2.52 (s, 3 H), 2.30 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.4, 140.4, 136.2, 135.3, 135.2, 135.1, 135.0, 132.6, 132.5, 130.9, 130.2, 130.1, 129.1, 128.3, 128.2, 128.1, 127.6, 127.3, 127.2, 127.1, 126.2, 122.7, 119.9, 110.3, 55.2, 20.5, 20.4, 20.2, 20.1. HRMS (ESI): *m*/*z* calcd for $[C_{31}H_{28}ONa]^+$: 439.2038; found: 439.2036.

(20) **Dibenzochryenes 4aa and 4ab; General Procedure**: A dried flask was charged with 9,10-disubstituted phenanthrene (0.4 mmol), $CuCl_2$ (270 mg, 2.0 mmol) and $AlCl_3$ (267 mg, 2.0 mmol) under argon, and CS_2 (5 mL) was added by a syringe. The mixture was stirred at r.t. until the reaction was complete. The mixture was diluted with CH_2Cl_2 and filtered through a plug of silica gel. The solvents were then removed under reduced pressure to provide a crude product, which was further purified by silica gel column chromatography (silica gel, PE–EtOAc).

Palladium-Catalyzed Annulation of 2,2′-Dibromobiphenyls with Alkynes; Synthesis of Functionalized Phenanthrenes and Dibenzochrysenes: A palladium-catalyzed annulation process of 2,2′-dibromobiphenyls with alkynes for the synthesis of functionalized phenanthrenes was realized. The electron-deficient heteroaromatic-substituted acetylenes are capable of the annulation process. Thiophene-fused and pyridine-fused PAHs can also be synthesized easily. This methodology also provides a highly efficient and low-cost approach to dibenzochrysene derivatives starting from simple commercially available reactants in two steps.